

# Expanding the Analyte Set of The JPL Electronic Nose to Include Inorganic Compounds

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## ABSTRACT

An array-based sensing system based on 32 polymer/carbon composite conductometric sensors is under development at JPL. Until the present phase of development, the analyte set has focused on organic compounds (common solvents) and a few selected inorganic compounds, notably ammonia and hydrazine. The present phase of JPL ENose development has added two inorganics to the analyte set: mercury and sulfur dioxide. Through models of sensor-analyte response developed under this program coupled with a literature survey, approaches to including these analytes in the ENose target set have been determined.

## INTRODUCTION

An electronic nose to be used as an anomalous event detector such as a chemical spill or leak in crew habitat in spacecraft has been under development at JPL for the past several years. This sensing system, the JPL Electronic Nose (ENose), is under development as an array-based sensing system which can run continuously and monitor for the presence of toxic chemicals in the air in real time. The sensing array in the JPL ENose is made from polymer-carbon composite sensing films [1-5], based on initial sensing film studies done in the Lewis group at Caltech [6, 7]. These conductometric sensing films are made from commercially available insulating polymers which are loaded with carbon black as the conductive medium. In the device designed and built for crew habitat air monitoring, a baseline of clean air is established, and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors is deconvoluted, and chemical species to which the device has been trained are identified and quantified by using a set of software analysis routines developed for this purpose.

When the device is operating, air is pumped from the surroundings into the sensor chamber. The air is directed either through an activated charcoal filter which is put in line to provide clean air for baseline data, or

though a dummy-filter of glass beads which is put in line to provide a pressure drop similar to that in the charcoal filter. A solenoid valve can be programmed to open the path to the charcoal filter and provide clean airflow for a programmable period of time at programmable time intervals; otherwise, the air is directed through the glass beads. Air then enters the sensing chamber, and resistance is measured. The Second Generation JPL ENose is shown in Figure 1 and a block diagram of the

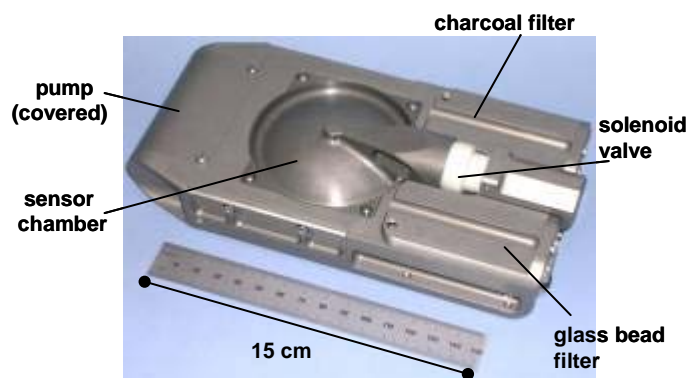


Figure 1: The Second Generation JPL ENose.

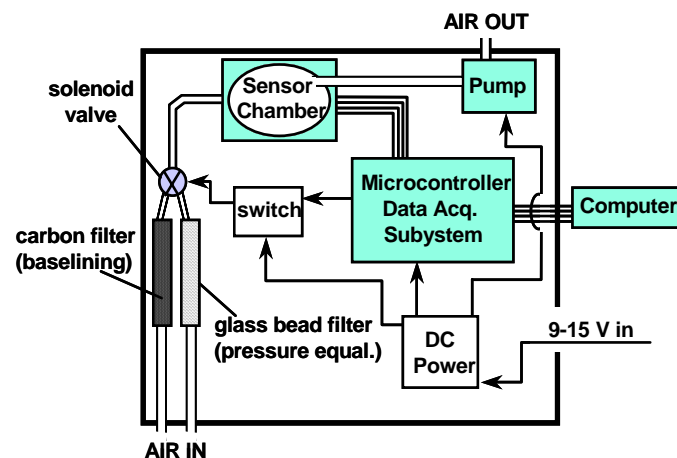


Figure 2: Block diagram of JPL ENose layout.

device layout is shown in Figure 2.

Until the present phase of development, the analyte set for event monitoring has focused on organic compounds (common solvents) and a few selected inorganic compounds, notably ammonia and water. Recently, NASA has recognized a need to detect two inorganic species in the breathing atmosphere of spacecraft. These species are elemental mercury vapor and SO<sub>2</sub>. These are chemicals of concern because they may be released in anomalous event scenarios. Mercury is found in some lighting, and it could be released into the air if lights were to break. SO<sub>2</sub> may be released as a breakdown product of SOCl<sub>2</sub> from a leaking or burst lithium-thionyl chloride battery. The detection goal in this development effort is 1 part-per-million (ppm) SO<sub>2</sub> and 10 parts-per-billion (ppb) Hg at atmospheric pressure.

Regenerable sensors which require no consumables for Hg and SO<sub>2</sub> require significantly different materials and conditions than have been built in to the JPL ENose. It is our goal to incorporate sensors which will not require major modifications in the device design or in the transduction method. Materials must be selected to provide conductometric sensors which can be regenerated without harming the sensors already selected for the organic analytes, as we must ensure that no capabilities are lost in adding the ability to detect, identify and quantify these analytes. In addition, we must ensure that exposure to either Hg or SO<sub>2</sub> will not damage the polymer-carbon composite sensors already in use, or, if it appears that some sensors will be damaged, we must replace them with other, equivalent, sensors.

This paper discusses our approach to selecting organic and inorganic materials to use as additional or replacement sensing materials in the ENose sensor array. We also discuss the sensing conditions necessary for reliable detection of these inorganic species and for regeneration of the sensors. In addition to selection of new materials to make sensors which will respond to Hg and SO<sub>2</sub>, we must ensure that the sensors which do not respond to these analytes are not poisoned and that all sensors can be used multiple times to detect all target analytes reliably.

We have approached the selection of materials and sensing conditions for Hg and SO<sub>2</sub> by modeling the binding energy of these potential contaminants with the polymer-carbon composite sensors that are used in the Second Generation JPL ENose and by reference to the literature on sensing these materials. The results of modeling polymer-carbon composite sensor response to these two analytes and of our literature search are described in the following sections.

## SENSOR-ANALYTE RESPONSE MODELING

**MODEL OF SENSOR-ANALYTE INTERACTION** - We have developed two approaches to modeling the sensing film-analyte interaction. In the first approach,

we calculate an energy of interaction between the monomer and the analyte [8, 11]. This is a rapid approach which is based on thermodynamic and electronic characteristics of the monomer and the analyte. The second approach is a more complete model of sensing film-analyte interaction, which takes account of the interaction energies among the polymer, carbon black, analyte, and water [8, 9]. Modeling is done using Cerius2 software.

To construct a polymer-carbon black composite model based on the experimental formulations, a polymer box of appropriate density is created, then carbon black modeled as uncharged naphthalene rings (with no hydrogens) is inserted into the box using a random cavity search in the polymer matrix. An equilibrium composite structure is obtained using a combination of molecular mechanics and molecular dynamics simulation techniques.

When the polymer-carbon black composite is equilibrated, interaction energies between one analyte molecule and the composite are calculated at 300 K using the SORPTION module in the Cerius2 software. The contributions to the total interaction energy between an analyte and the composite are its interactions with the polymer chains, carbon black, and other compounds, such as water that may be present. The simulation program generates random points in the composite model and attempts to insert the analyte molecules. Insertion attempts that involve the overlapping of the analyte molecule with the composite structure are discarded. For each composite-analyte interaction, 2–3 million simulations (analyte insertions) were run and the average energy of composite-analyte interactions was calculated at the end of the simulation.

After the sensor analyte interaction energy is calculated, it is used as a screening tool to determine whether there is any possibility of sensor response to a given analyte. Although the result is a quantitative interaction energy, or in the case of the composite model the heat of sorption, application of this method allows only a qualitative judgment of the possibility of sensor response.

In an effort to predict the magnitude of response of analytes to polymer-carbon composite sensors, we have used Quantitative Structure-Activity Relationships (QSAR), a semi-empirical multivariate statistical approach, to correlate measured sensor activity with sensor and analyte properties [10]. The QSAR model is obtained using a combination of variables (descriptors) that describe both the analyte properties as well as the sensing film-analyte interactions. In our work, the sensor activity for a given analyte is defined as the coefficient, A<sub>1</sub>, which is correlated to the sensor response as  $y = A_1x + A_2x^2$ , where x is the concentration of analyte. A<sub>2</sub> is generally three to five orders of magnitude smaller than A<sub>1</sub>. Hence a low value of coefficient A<sub>1</sub>, would imply weak or no sensor response to a given analyte [4].

MODELED RESPONSES OF Hg AND SO<sub>2</sub> – Initial calculations of sensor-analyte interaction energy and of heat of sorption indicated that the interaction of Hg and SO<sub>2</sub> with the polymer-carbon composite sensors used in the JPL ENose would be very small and would not be likely to result in a measurable response on the sensors. We compared the interaction energies of Hg and SO<sub>2</sub> to that of CO<sub>2</sub>. This approach predicts a similarly small interaction energy for CO<sub>2</sub>. CO<sub>2</sub> is not detected by the polymer sensors used here (earlier reports of CO<sub>2</sub> detection [1] were later determined to be pressure spikes), and it was assumed that a similar interaction energy would result in a similar sensor response.

Following these initial calculations, the sensor activity of polyethylene oxide-carbon films (PEO-CB) to the inorganic analytes CO<sub>2</sub>, SO<sub>2</sub> and Hg was predicted based on a QSAR generated equation developed for organic solvents [11] and ammonia. This equation was able to predict the response of this sensor to ammonia with a high degree of accuracy. A detailed explanation of the selection and optimization of the descriptors, sensor activity equation form and type as well as other statistical considerations can be found elsewhere [9]. In brief, descriptors were developed using empirical and semi-empirical predictive methods such as Quantitative Structure-Property Relationships (QSPR) as well as molecular modeling tools.

The QSAR-derived expression for the activity of a polymer-carbon composite sensor made using polyethylene oxide predicts the activity of organic compounds with good correlation ( $r^2 = 0.86$ ). This expression is  $0.15E_{pa} + 0.11 HB_D^2 + .00024 MR^2$ , where  $E_{pa}$  is the calculated energy of interaction between polymer and analyte,  $HB_D$  is the number of hydrogen bond donor sites on the analyte and  $MR$  is molar refractivity of the analyte.

Molecular models to calculate the sensing film-analyte interactions for the polymer, carbon black, and analytes were developed using the commercial software Cerius<sup>2</sup> [12] on a Silicon Graphics O2 workstation. The Dreiding 2.21 force field [13] was used for the polymer and CO<sub>2</sub> and SO<sub>2</sub> molecules, while graphite parameters were

assigned to the carbon black atoms [14]. Elemental Hg was described using the Universal force field [15].

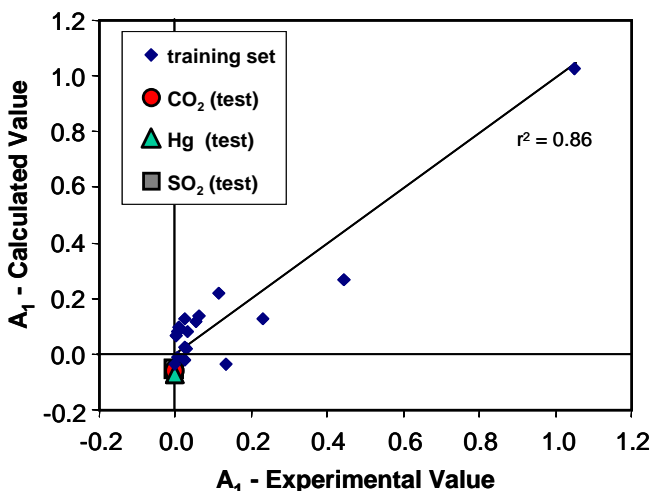
Application of the QSAR-derived expression for polyethylene oxide sensors supported the conclusion that the response of the polymer-carbon composite sensors used in the JPL ENose to the presence of Hg and SO<sub>2</sub> would be very small or immeasurable. Figure 3 shows a plot of calculated activity for several organic compounds and ammonia vs. measured activity for those analytes (diamonds). The point at 1.0, 1.0 represents the A1 value for ammonia; all other points are for organic molecules. Fitting only to the organic molecules does not change the equation significantly, although it does change the  $r^2$  value.

Figure 3 also shows the calculated activity for three inorganic analytes, Hg, SO<sub>2</sub> and CO<sub>2</sub>, plotted against zero. The activities of the inorganic analytes are clustered near 0, indicating that the response of polyethylene oxide sensors to those analytes would be very small. This approach is not meant to develop an A1 value for these compounds, but is meant to be used as a guide to whether the existing sensors can be expected to respond significantly to Hg and SO<sub>2</sub>. These predicted activities will be verified experimentally.

## LITERATURE SURVEY

SO<sub>2</sub> SENSORS – Several researchers have studied development of sensors to detect SO<sub>2</sub>, and some have addressed using polymer-based sensors to do so. There are potentiometric and amperometric SO<sub>2</sub> sensors which use solid oxide electrolytes such as alumina or zirconia [16, 17], but these electrolytes require operating temperatures in excess of 600° C and so would not be suitable for application to the JPL ENose. There are also reports of metal oxide based conductometric sensors which have been used for SO<sub>2</sub> detection [18-20]. Metal oxide sensors also require relatively high temperatures (400°C). They may be suitable for this application, but the high temperatures required would require a redesign of the hardware we would like to avoid, if possible. There are several researchers working in application of polymer-based sensors for SO<sub>2</sub> detection. Many of those sensors have been electrochemical (amperometric or voltammetric) [21-23], but there have also been several reports of mass uptake sensors which use polymers as the sensitive coating [24-29]. In addition, mass uptake sensors using organic (non-polymeric) [30] and inorganic coatings [31, 32] have been reported.

The sensor type which is most similar to the polymer-carbon composite conductometric sensors now used in the JPL ENose is the mass uptake sensor. In general, materials that can be used as sorbents for mass uptake sensors are good candidates for use as composites with carbon to make conductometric sensors, as the major sensing mechanism is based on volumetric swelling resulting from mass uptake [5].



**Figure 3:** QSAR calculated value for A1 coefficient for three inorganic analytes

It has been known since the 19<sup>th</sup> century that the Lewis acid SO<sub>2</sub> reacts readily with the basic amine groups, and so many coatings used for SO<sub>2</sub> detection based on mass uptake include amine groups [25]. Ranucci and co-workers [25, 26, 29] did extensive studies on variously functionalized poly-amidoamines (PAAs), polymeric bases of moderate strength. They found that several PAAs sorb SO<sub>2</sub> reversibly at room temperature or slightly elevated temperatures, that SO<sub>2</sub> sorption increased in the presence of moisture, and that CO<sub>2</sub>, another Lewis acid, was not an interferant up to 5000 ppm CO<sub>2</sub>. The lowest concentration studied by this group was 1 ppm SO<sub>2</sub>.

Other coatings used in mass uptake sensors include amino-silanes [24], sol-gel coatings of amino-siloxanes [27] and polymeric amino-functionalized polystyrenes stabilized by siloxane [28]. The sol-gel coating of amino-siloxanes was used to detect a few ppm of SO<sub>2</sub> at 30°C with good reversibility. The amino-functionalized polystyrenes detected 50 ppm SO<sub>2</sub> reversibly at 50-90°C. An organic coating of triethanolamine stabilized with boric acid [30] was also shown to sorb SO<sub>2</sub> reversibly below room temperature (12°C); 1 ppm SO<sub>2</sub> was detected in this work.

There have been reports of the use of inorganic CdS coatings as SO<sub>2</sub> sensors [31,32]. CdS is a semiconductor which is also used as an electrode in solid oxide SO<sub>2</sub> sensors. Early reports detected 10 ppm SO<sub>2</sub> reversibly on a conductometric sensor at rather high temperatures, 160°C with reversibility at 300°C [31]. Later researchers used CdS as a mass uptake coating and were able to detect concentrations as low as 200 ppb at 80°C, with complete regeneration several tens of times at 160°C [32].

**MERCURY VAPOR SENSORS** – Mercury is well-known to form an amalgam with gold and several other metals, including noble metals and aluminum. There have been several researchers who have reported sensors for detection of mercury vapor using thin films of gold and other noble metals as mercury capture surfaces [33-39]. These mercury vapor sensors have used a variety of transduction methods, including conductometric and mass-uptake methods.

The earliest reported mercury vapor sensors based on thin films of gold, in 1972, measured the change in resistance of the film [33] or used a gold film as a mass uptake surface [34]. Both methods are still reported as effective and regenerable Hg sensors.

Researchers have reported mercury vapor detection sensitivities as low as 100 parts-per-trillion (ppt) [33, 35], with the ability to regenerate the sensor hundreds of times by heating to temperatures between 150 and 200 °C using gold film resistors as detectors [35]. In addition, gold has been used as a coating on several different types of mass uptake sensors [36-39] based sensors. Mass uptake methods have reported measured

sensitivities to Hg vapor below 100 ppb in air [37, 39] with a calculated sensitivity as low as 20 ppb [39].

Besides gold, other metals including Ir, Pd, Pt, Rh and Al have been studied for their ability to form an amalgam with Hg [40- 43]. Hg vapor will amalgamate with thin films of these metals, resulting in a change in resistance in the film, and such films could be used similarly to gold as mercury vapor sensors.

However, amalgamation of Hg with a thin film of gold or another metal does not lead to a specific sensor for Hg. Other materials, such as water vapor and sulfur-containing compounds can also react with thin gold films, making it difficult to distinguish between responses to Hg and responses to other analytes. In order to avoid cross-sensitivity with water and sulfates, Mirsky *et al.* found that a selective filter could be made by coating a gold film with a self-assembled monolayer of hexadecanethiol, which was sufficient to exclude water and sulfate while allowing mercury and iodine to reach the gold layer [44].

Other researchers have taken an approach with mass uptake sensors where various coatings were studied to determine which would be the optimum for Hg uptake [45]. That work considered several polymers used as stationary phases in gas chromatography as well as mixtures of PdCl<sub>2</sub> with tetrahydroxyethyl-ethylenediamine (THEED). PdCl<sub>2</sub> reacts readily with Hg to form HgCl<sub>2</sub>, a very stable compound, and can be used to trap Hg [44]. McNerny [33] found that a filter of glass wool and PdCl<sub>2</sub> was sufficient to exclude Hg vapor from a sample stream. Ruys *et al.* found that the optimum coating to capture Hg vapors is a 1:1 mixture of PdCl<sub>2</sub> and THEED [45], with good desorption at 35°C.

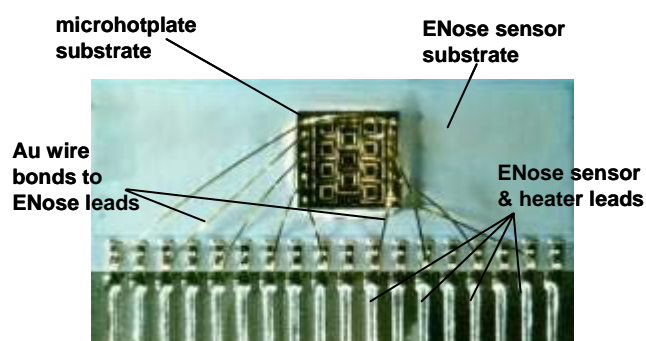
## SELECTION OF MATERIALS

Materials to be selected in order to expand the analyte set of the JPL ENose to include Hg and SO<sub>2</sub> include active sensing surfaces, materials used in the sensing chamber for attachment and electrical contact, materials used in the pneumatic system and flow path, and filter materials.

**HIGH TEMPERATURE SENSORS** - As the JPL Electronic Nose has been previously designed and demonstrated using conductometric sensors, where change in resistance in the sensing film is measured and correlated with analyte identity and concentration, our desire is to continue to use this transduction method. Use of this method would minimize the need for redesign of the electronic circuitry and mechanical design of the device. Review of the literature has shown that regeneration of conductometric sensors which are sensitive to Hg and SO<sub>2</sub> will require heating capabilities not now incorporated in the JPL ENose (sensors can now be heated to 36-40°C). We plan to replace eight of the 32 sensors now in the array with higher-temperature

sensors on which conductometric sensing films can be deposited.

Because of the need for higher temperatures than are now in use in the JPL ENose for both regeneration and sensing in SO<sub>2</sub> and Hg sensitive sensors, and because of the need to keep the power budget of the device as low as possible, we intend to use microhotplate sensors provided by Aerospace Corp. [46] as a direct replacement for one of the eight sensor substrates in the current device. Figure 4 shows a concept for the planned replacement. A microhotplate (MHP) substrate will be attached to a substrate that will fit into the space used by one ENose sensor substrate. The MHP sensor and heater leads will be wire-bonded to the ENose sensor substrate leads; the assembly and will fit into the contact space in the ENose sensor chamber.



**Figure 4:** Planned replacement scheme to add MHP sensors to the existing JPL ENose.

Replacement of eight polymer-carbon composite sensors with eight MHP sensors in the array will not raise the power requirements of the device significantly. The MHP sensors heat at approximately 11°C/mW; heating eight sensors to 200°C from 25°C will require less than 150 mW power.

In both the existing sensor configuration and in MHP sensors, metallic contacts and leads are exposed to the sampled environment. Contacts and leads are made from gold, aluminum, and tin, and lead-tin solder. To ensure that conductivity in wires, wire-bonds, contacts and leads are not affected by amalgamation with mercury or sorption of SO<sub>2</sub>, all exposed metal will be coated with a suitable lacquer or other inert coating.

**SO<sub>2</sub> SENSITIVE MATERIALS** – Based on the literature review of SO<sub>2</sub> sensors, four MHP sensors will be made as a sub-array to detect SO<sub>2</sub>. Initial experiments will use two selected functionalized poly-amidoamines [25, 29], and an amino-siloxane [27] which have been loaded with carbon black to make them conductive, and CdS [32]. It is not known whether the amine functionalized polymers can be made into a conducting polymer-carbon composite film, but hydrogen-bond basic polymers already in use in the JPL ENose [5], such as polyvinylpyrrolidone and polyamide resin, show good response to several compounds, and indicate that other

amine-containing polymers can be used in the same way.

On testing the SO<sub>2</sub> designated polymers for response, we will also observe responses in all other polymers to determine whether they respond to SO<sub>2</sub> and whether they can be regenerated at ~40°C accessible to the non-MHP sensors.

**MERCURY SENSITIVE MATERIALS** – The abundance of literature on using gold films as Hg detectors, and the ability to regenerate such films by heating to 150-200°C, indicates that a gold film sensor would be a good choice as part of a sub-array for mercury sensing. However, other chemical species, especially sulfur containing compounds, also sorb to or react with gold surfaces, so more than one type of sensor will be necessary for unambiguous identification and quantification of mercury. If it is found that SO<sub>2</sub> or other trace background gases are interferants for Hg, use of a filter such as that described by Mirsky *et al.* [44] will be considered.

Recently, several researchers have investigated the use of metal-polymer composite films [47-49] and metal-decorated polymer nanofibers [50]. Sensors made from these types of materials are appealing as possible additions to the sensor set of the JPL ENose, as they combine conducting films of polymers, as used in the present ENose, with the possibility of the addition of noble metals which will bind Hg. We have had only moderate success with replacing carbon in the polymer-carbon composite films with noble metals in our laboratory, but the reported methods incorporate metal into the film or on the nanofibers during the polymerization step. The polymers used in these cases are electronically conducting polymers. Conducting polymers (without metals) have been used as sensing elements in sensor arrays [51]. Conducting polymer sensors with metal inclusions added to the sensor set will be useful in the array of polymer sensors for detection of organic compounds, and will also respond to Hg through amalgamation of the noble metal.

Based on this information, four MHP sensors will be made as a Hg sub-array for initial testing. Two of these sensors will be thin films of noble metal – gold and palladium or platinum. Two sensors will be polymer – polymer composites.

**REGENERATION OF SELECTED MATERIALS** - In the polymer-carbon composite sensors now used in the JPL ENose, after response to organic solvents the sensor returns to baseline several seconds to a few minutes when the source of analyte is removed. This is not the case with Hg or SO<sub>2</sub>.

Gold films used as Hg sensors can be regenerated by heating the film to 150-200 °C for several minutes in a flow of clean air [52]. In application of this method to an air quality monitor, the dosimeter qualities of gold film sensors must be taken into account in determining the concentration of Hg vapor in the air. Because the flow of



air through the sensing chamber is controlled by a pump operating at a constant flow rate, it will be possible to calculate the concentration of Hg vapor in the air as the amalgam builds on a gold film. It will be necessary to program a regeneration step into the operating software after a mercury event has been detected.

**BASELINING FILTER** - The JPL ENose baselines using an activated charcoal filter [1-3]. In order to ensure that any Hg vapor in the air is removed from the cleaned air baselining stream, PdCl<sub>2</sub> or gold mesh will be added to the filter. SO<sub>2</sub> is adequately captured on the charcoal filter.

**FLOW PATH** – The flow path in the ENose is primarily hard anodized aluminum, which is inert to both Hg and SO<sub>2</sub>. The wetted portions of solenoid valve are made from polyetheretherketone (PEEK), and the o-ring seals are made from Kal-Rez. Both these materials are chemically compatible with Hg and SO<sub>2</sub> in the dilute concentrations needed in this application.

## CONCLUSION

Modeling of analyte sensor response leads to the conclusion that the polymer-carbon black composite sensors now used in the JPL ENose will have very small or negligible response to the presence of the two inorganic species mercury and SO<sub>2</sub>. A literature search has resulted in a plan to replace eight of the 32 polymer-carbon composite sensors in the JPL ENose with MHP sensors. Four of those MHP sensors will be a sub-array directed toward SO<sub>2</sub> detection, with two amine functionalized PAA sensors, an amino-siloxane sensor and a CdS film sensor. It is expected that the organic sensors will respond to several other analytes. The remaining four MHP sensors will be a sub-array directed toward Hg detection, but it is expected that some or all of the sensors in that sub-array will respond to other species as well as Hg, particularly SO<sub>2</sub>. MHP sensors have been selected because it will be necessary to heat the sensors well above 100°C for reliable regeneration. As yet, there are no data available generated in our laboratory for the selected sensor materials.

## ACKNOWLEDGMENTS

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